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New Zinc-*bis*(dialkylamides) Potentially Usable as Site-Selective Dopants
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by

William S. Rees, Jr. and Oliver Just

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**NEW ZINC BIS(DIALKYLAMIDES) POTENTIALLY USEABLE AS
SITE-SELECTIVE DOPANTS FOR P-TYPE ZnSe**

WILLIAM S. REES, JR. AND OLIVER JUST

**Department of Chemistry and Materials Research and
Technology Center
The Florida State University
Tallahassee, Florida 32306-3006**

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WILLIAM S. REES, JR. AND OLIVER JUST.

MS: B-164, Department of Chemistry and Materials Research and Technology Center, The Florida State University, Tallahassee, Florida, 32306-3006.

ABSTRACT

In earlier work, the effective utilization of $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$ as a site-selective dopant for the production of p-type ZnSe by OMVPE was demonstrated. Several new zinc-*bis*(dialkylamides) of the general form $(\text{R})(\text{R}')\text{NZnN}(\text{R}'')(\text{R}''')$ now have been prepared. They have been characterized by ^1H - and ^{13}C -NMR, GC/MS and elemental analysis. Vapor pressures and gas phase decomposition profiles have been examined. Correlations of vapor pressure and structure are discussed for this series of compounds. A mechanism for the site-selectivity observed in the incorporation of nitrogen is proposed.

INTRODUCTION

Among the various potential candidates of semiconducting materials for utilization in optoelectronic and electroluminescent devices operating in the blue region of the visible electromagnetic spectrum, p-type ZnSe recently has emerged as a promising leading contender for near-term practical applications.¹⁻⁶ Therefore a variety of efforts have been undertaken to gain access to suitable, readily-prepared and purified precursors for the production of this desired composition. Recently, we demonstrated that compounds of the general form $(\text{R})(\text{R}')\text{NZnN}(\text{R}'')(\text{R}''')$ retain a zinc-nitrogen bond during their decomposition to produce a thin film of N-doped ZnSe by OMVPE (organometallic vapor phase epitaxy).⁷ As a consequence of these promising results, an investigation into the scope of the process was initiated.⁶ In previous reports^{8,9} it was shown that acceptable results could be achieved either with the homoleptic symmetrical $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$ or the homoleptic unsymmetrical $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3][\text{C}(\text{CH}_3)_3]\}_2$ regarding their suitability as potential dopant sources for the preparation of high quality p-type ZnSe thin films by OMVPE. This success is based on the selective incorporation of nitrogen atoms on the native selenium lattice site, which is enforced by the lack of an appreciable antisite defect

density for zinc atoms in the native ZnSe lattice. Thus, in the instances when the Zn-N bond of the precursor dopant molecule is retained intact throughout the deposition process, the nitrogen atom has an enforced residence on a lattice site adjacent to a native zinc location, *i.e.*, in an electronically active position on a native selenium atom lattice site. The proposed mechanism for the gas phase decomposition profile of the heteroleptic $\text{Zn}\{[\text{N}(\text{Si}(\text{CH}_3)_3)_2][\text{N}(\text{Si}(\text{CH}_3)_3)(\text{C}(\text{CH}_3)_3)]\}^{10}$ provided for the existence of the desired penultimate structural fragment "RNZn". Subsequent to undergoing a β -hydride elimination by the appropriate alkyl group, observation of co-product olefin and "HNZn" significantly contributed to the overall understanding of the nitrogen incorporation process occurring during the epitaxial growth of p-type ZnSe. As a consequence of the limited volatility of these prior precursors, a priority was given to extend these studies to other diverse substituted zinc-*bis*(dialkylamides) and an examination of their employment as possible dopants by OMVPE.

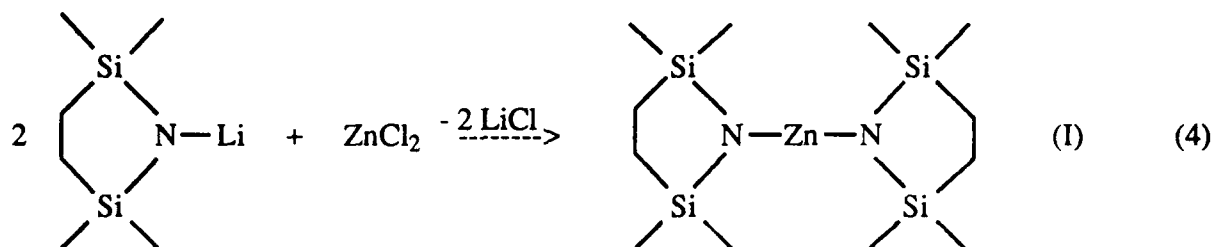
EXPERIMENTAL

An effective access to compounds depicted by the general formula $\text{Zn}[\text{N}(\text{R})(\text{R}')_2]$ is provided by a synthetic route¹⁰ comprising the salt elimination reaction between one equivalent of zinc dichloride and two equivalents of alkali metal dialkylamide under inert gas (eq. 1) yielding the target molecules as stable compounds. The preparation of the alkali metal dialkylamide salt was accomplished by treating the corresponding primary amine with trimethylchlorosilane (eq. 2) and deprotonation of the generated trimethylsilylalkylamine with butyllithium or potassium hydride (eq. 3a or 3b):



$\text{R} = \text{Si}(\text{CH}_3)_3$; $\text{R}' = \text{Et}, i\text{-Pr}, n\text{-Pr}, t\text{-Bu}, c\text{-Hex}, \text{Ph}.$

After demonstrating the usefulness of the homoleptic symmetrical $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$ as a dopant for deposition of p-type ZnSe films, attention was focused toward performing experiments in order to obtain a zinc-*bis*(dialkylamide) containing the closely related tetramethyldisilaazacyclopentane-ligand as a minor modification of the *bis*(trimethylsilylamido)-ligand (eq. 4). The anticipation in seeking this compound was to increase the stability of the intrinsically labile zinc-nitrogen bond under normal conditions by potentially protecting it from nucleophilic oxygen attack. Additionally, the retention of this desired interaction throughout the thermal decomposition is ensured by primary elimination of the fragment $[\text{Me}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2^+]$.

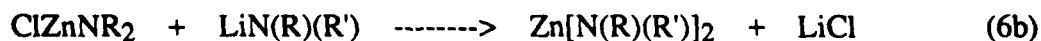


Based on encouraging results obtained during the investigation with *bis*(triorgano-silylsubstituted)amide derivatives of zinc(II), an effort was instigated to examine the potential for extension of a comparable synthetic and purification scheme to encompass *bis*(diorgano-silylsubstituted)amide analogs. As an initial entry into this new class of compounds, the homoleptic derivative of *bis*(dimethylsilyl)amide was selected. Examples of this new class of compounds were isolated by application of an analogous synthetic route (eq. 5) to that depicted in eq. 1. It was postulated that replacement of one of the methyl groups on silicon by a hydrogen atom might have a substantial impact on the properties of this next generation of zinc compounds, particularly with respects to enhancing their vapor pressures.



$\text{R} = \text{Si}(\text{H})(\text{CH}_3)_2$; $\text{R}' = i\text{-Pr}, t\text{-Bu}, \text{Si}(\text{H})(\text{CH}_3)_2$.

Additionally, capitalizing on a previously developed and described method⁹ it was possible to obtain a new heteroleptic zinc-*bis*(alkylsilylamide); ($\text{R} = \text{Si}(\text{CH}_3)_3$, $\text{R}' = i\text{-Pr}$), (eq. 6a and 6b):



RESULTS AND DISCUSSION

The isolation and purification process for these new generations of zinc-*bis*(dialkylamide) compounds has revealed several characteristic and unconventional properties. Following eq. 1 the isolated compounds are colorless and viscous distillable liquids ($R = \text{Et}$, *i*-Pr, *c*-Hex, Ph) as well as ambient condition colorless solids ($R = t\text{-Bu}$, *n*-Pr). The highest vapor pressure to date is displayed by the *i*-propyl representative (b.p. = 56°C / 0.05 Torr). This property diminishes dramatically with increasing size of the ligands: $n\text{-Pr} > t\text{-Bu} > c\text{-Hex} > \text{Ph}$, but remarkably the smallest member of this group of compounds, represented by the ethyl derivative, exhibits in a discrepancy with the expected trend an extremely decreased volatility. This result indicates that the corresponding zinc compound is most likely not a monomer, which is consistent with ^1H -NMR studies. An additional feature is that the heaviest substituted zinc amides ($R = c\text{-Hex}$, Ph) are colorless and viscous oils, while zinc amides carrying medium size ligands such as *t*-Bu and *n*-Pr are solids. The analogous synthesis of compounds containing the dimethylsilyl group (eq. 5) revealed that the isolated *t*-butyl product possesses (in comparison with the corresponding trimethylsilyl compound) an uncomparably enhanced vapor pressure. On the contrary the volatility of the *i*-propyl as well as the dimethylsilyl representative (both are highly viscous oils), is decreased greatly.

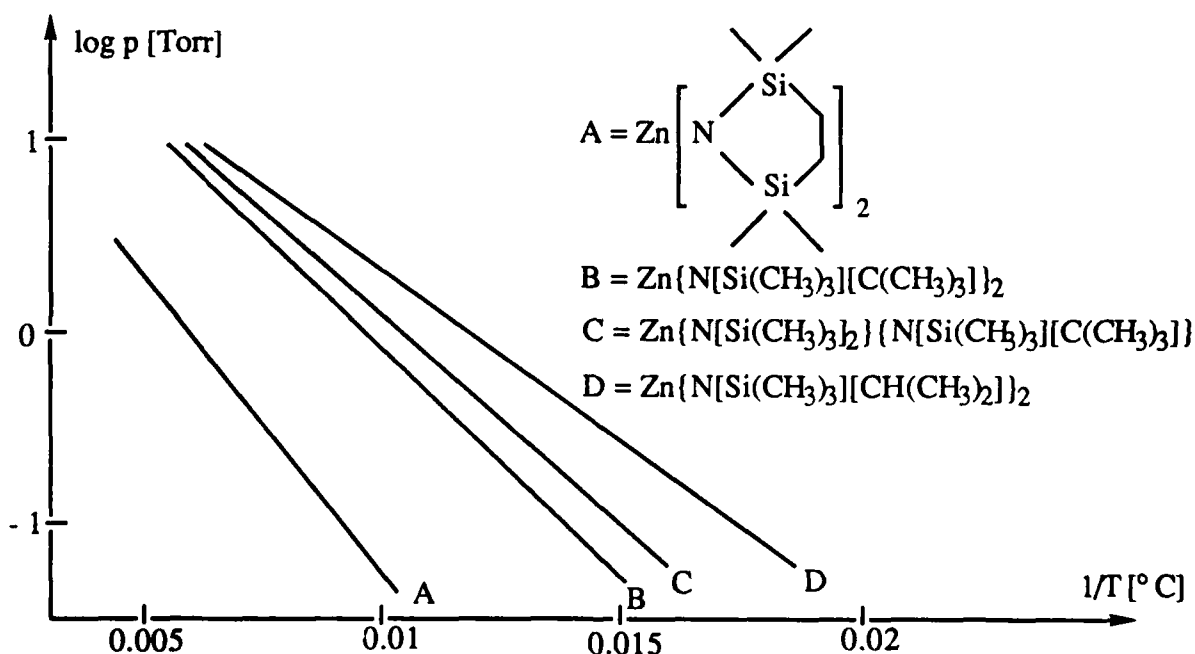


Fig. 1: Vapor pressure profiles determined for a series of various zinc-*bis*(amides).

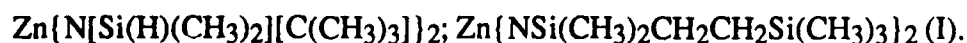
By the established method (eq. 6a and 6b) separated new heteroleptic *i*-propyl species is distinguished by its extreme volatility which only slightly varies from that found for the analogous homoleptic product. The symmetrical zinc-*bis*(dialkylsilylamide) (I) generated by the successful execution of the reaction outlined in eq. 4 turned out to be a colorless crystalline solid (m.p. = 47°C) and under normal conditions for a limited time the most environmentally stable zinc compound prepared in this study. However, compared with $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$, it displays a negligible depressed vapor pressure.

The investigated mechanisms of processes occurring in the gas phase during thermal decomposition of three alternate types of zinc-*bis*(amide) examples show in two cases the presence of the thermodynamically stable byproduct NR_3 as a driving force for formation of "HNZn" and elimination of " ZnN_2 ", respectively. Since experiments conducted on the heteroleptic unsymmetrical zinc amide⁹ have revealed the existence of site-selective deposition of p-type ZnSe in conjunction with essential structural fragments NR_3 , RNZn and "HNZn" our investigations on the produced compounds concentrated on searching for these important fragments. The detailed studies of the gas phase decomposition profile of the heteroleptic $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}\{\text{N}[\text{Si}(\text{CH}_3)_3][\text{C}(\text{CH}_3)_3]\}$ have confirmed in the preliminary investigations⁹ reported pattern containing $\text{N}(\text{TMS})_3$ and $^t\text{BuNZn}$ and subsequent to β -hydride elimination, the presence of "HNZn". On the contrary, those signals are absent in the mass spectrum of the homoleptic unsymmetrical $\text{Zn}\{\text{N}[\text{Si}(\text{CH}_3)_3][\text{C}(\text{H})(\text{CH}_3)_2]\}_2$, which is consistent with the requirement for a bimolecular mechanistic pathway. The most characteristic observed fragments which have been split off the parent peak can be interpreted as: $[i\text{-Pr}_2\text{N}^+]$ and $[i\text{-PrNSiMe}_3^+]$.

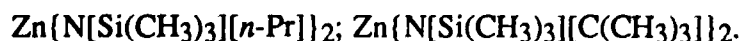
Due to the well-known stability of the fragment $[\text{Me}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2^+]$, the elimination of " ZnN_2 " has been observed in the decomposition pattern of the homoleptic symmetrical zinc amide depicted in eq. 4. We note, that in other work, erbium[*tris*(trimethylsilyl)amide] has been employed successfully in the OMVPE growth of Er-containing electronic materials.^{11,12}

The experiments which were carried out to date on the available zinc-*bis*(amides) allow the arrangement into three categories regarding their potential suitability for OMVPE:

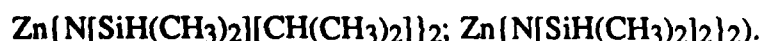
Precursors which should have utility in the epitaxial growth of p-type ZnSe:



Products which probably are well suited to achieve this goal:



Compounds with chemical and physical properties which most likely will not serve this purpose as well as the examples enumerated above:



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